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SWELLABLE HOT-MELT ADHESIVE

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Abstract

Thermoplastic materials on the basis of a water-insoluble constituent of one or more thermoplastic copolymers and one or more resins with a saponification value and a water-soluble or water-dispersible constituent and a water-swellable constituent of the superabsorber class are suitable as water-swellable hot-melt adhesives. Said water-swellable hot-melt adhesives can be preferably used to produce watertight constructions, specially longitudinally watertight cable constructions.

The invention concerns a water-swellable thermoplastic compound for gluing and coating made from a water-insoluble component, a water-soluble or water-dispersible component and a water-swellable component. The invention additionally concerns

the use of these thermoplastic materials to make watertight constructions, especially to make longitudinally watertight cable constructions.

With a large number of constructions such as pipes and especially cables that are laid in the ground or under water, there is the need to protect these constructions against the penetration of water at joints and bonding sites or if there is damage to their outer casing. In particular, power and/or telecommunication cables are long-term capital investments, whose operational security must be ensured for a very long period of time. If there are damages to the outer insulation and/or at faulty joints water will penetrate into the interior of cable constructions of this kind and this water encroachment can lead to a considerable damage to the cable. In this case there can be rapid spread of the water along the long axis of the cable and this can make a cable damaged in this way unusable over long stretches.

To prevent the penetration of water into constructions of this kind water-swellable sealing materials or sealing constructions have been in use for a fairly long time. JP-A-58-215334 (83) describes in general form heat-hardenable sealing materials made from rubbers and a water-swellable polyurethane resin that is based on ethylene oxide/propylene oxide copolymers.

In accordance with the state of the art, multilayer sealing systems are used to make longitudinally watertight power or telecommunications cables. For example, in "Draht und Kabelpanorama," May-June-July, 1988, pages 64 to 68, W. Scahäfer and P. Graber describe swelling flowable substances made from an extremely homogeneous swelling layer consisting of a mixture of

a synthetic hydrogel-forming agent (swellable powder) with chemically pure cellulose pulp as filler and a high-mechanical-strength carrier layer of polyester fibers with polyester filaments as an additional reinforcing element. These two layers are bonded to each other without the use of low-melting thermoplastics by means of high pressure and temperature. Then swellable wrappings are made from nonwoven materials or yarns of this kind and are used to wrap the conductor bundle, optionally in combination with a plastic inner jacket.

EP-A-188,959 describes a multilayer sealing ribbon consisting of a carrier of paper, textile materials or plastics, which is coated with a layer of a water-swellable polymer powder and a water-soluble binder as well as optionally a surfactant.

US-A-5,070,875 describes cable constructions in which the layer that is intended to prevent the encroachment of water by swelling consists of a multilayer laminate. This laminate consists of two carrier strips of hydrophobic material such as polyester. A water-swellable polymer or copolymer of the "superabsorber" type is laid between these two carrier strips.

US-A-5,188,883 describes a multilayer composite structure of a metal ribbon as one layer and a layer of a swellable water-blocking material, where the two layers and surfaces are bonded with the aid of an adhesive.

The use of the above-mentioned multilayer composite material to make longitudinally watertight cable constructions is expensive and cost-intensive because of the large number of process steps that are involved. For this reason there was a need to make available products that enable a simpler manufacture of longitudinally watertight cable constructions.

In accordance with the invention this task is solved by a thermoplastic material that is swellable with water and that essentially consists of three components:

A) A water-insoluble component containing at least one water-insoluble polymer or copolymer and at least one other essentially water-insoluble resin.

B) A water-soluble or water-dispersible component, where this component contains at least one water-soluble or water-dispersible oligomer and/or polymer or copolymer,

C) A water-swellable component, which consists of a water-swellable homo- or copolymer,

where components A, B and C are homogeneously intermixed. The term "homogeneously intermixed" in the sense of this invention should be understood to mean that the matrix of the material does not have any macroscopic inhomogeneities. This does not mean that different phases consisting of the water-insoluble component and the water-soluble component or water-swellable component exist in the microscopic region. In particular, homogeneously intermixed is not supposed to mean the water-swellable homo- or copolymer of component C is supposed to be present in a molecularly dissolved form in one or both of the other components.

These water-swellable thermoplastic materials thus are hot-melt adhesives that can be used in particular in cable constructions.

As the water-insoluble homo- or copolymer of component A basically all of the thermoplastic polymers that are known for use in hot-melt adhesives can be used, for example, polyamides, copolyamides, polyaminoamides, polyesters, polyacrylates, polymethacrylates, polyolefins as well as, in particular,

ethylene/vinyl acetate copolymers or mixtures of one or more of these polymers should be mentioned.

As an additional resin in component A all of the substantially known tackifying resins, with the exception of the pure hydrocarbon resins, can be used to increase the adhesiveness of the melt. The resins to be used in accordance with the invention thus have a saponification number that is not 0. Especially suitable in this regard are the various colophonium derivatives, i.e., in particular, the resin esters of abietic acid, but other polyterpenes as well as terpenephenol resins are also suitable.

A large number of water-soluble or water-dispersible oligomers or homo- or copolymers are suitable for the constituents of component B. Examples that may be mentioned include polyethylene glycols in the molecular weight range between 2400 and 20,000, polyvinyl methyl ether, polyvinylpyrrolidone, copolymers of vinyl methyl ether or vinylpyrrolidone, polyvinyl alcohols, water-soluble or water-dispersible polyesters or copolyesters, water-soluble or water-dispersible acrylate polymers.

The water-swellable component C can be formed by all of the relevant homo- and/or copolymers that, as hydrophilic materials, absorb large amounts of water and are capable of retaining it even under pressure without immediately being dissolved in the water. Hydrophilic materials of this kind are also known as "superabsorbers." Examples that may be mentioned here are graft copolymers of starch or cellulose with acrylonitrile, acrylic acid or acrylamide, carboxymethylcellulose, maleic acid anhydride/poly-α-olefin copolymers, polyacrylamide, polyacrylic

acid and salts of polyacrylic acid as well as possibly copolymers of acrylic acid or acrylamide with acrylate esters.

In each case according to the use of the hot-melt adhesives in accordance with the invention they can have properties of surface tackiness or can have tackfree surfaces for the so-called "blockfree" versions. The last mentioned compositions contain substantially known wax additives, in particular bisstearamide waxes. In addition, both versions of the hot-melt adhesives in accordance with the invention can contain substantially known commercially available stabilizing agents that ensure temperature stability of the formulations.

Especially preferred surface-tacky swellable hot-melt adhesive compositions contain the following constituents:

15 to 45% by weight resin esters or terpene phenol resins

15 to 40% by weight thermoplastic copolymer, in particular ethylene vinyl acetate copolymers,

5 to 20% by weight acrylate copolymers

5 to 30% by weight polyethylene glycols,

5 to 15% by weight polyvinyl ethyl ethers, water-soluble or water-dispersible acrylate polymers or water-soluble or water-dispersible copolyesters

15 to 50% by weight powdered polyacrylic acid salt, polyacrylamide or similar powdered superabsorbers

0.2 to 2.0% by weight commercial stabilizing agents.

Especially preferred swellable hot-melt adhesive formulations in the block free version contain:

15 to 45% by weight resin esters, terpene phenol resins or the like

15 to 4% by weight thermoplastic (co)polymer, especially ethyl/vinyl acetate copolymer

5 to 25% by weight polyethylene glycols

15 to 50% by weight powdered superabsorber, in particular a polyacrylic acid salt

0.2 to 2.0% by weight stabilizing agent

0.5 to 5.0% by weight waxes, in particular ethylene bisstearamide.

These water-swellable hot-melt adhesives in accordance with the invention are suitable, for example, as coating for metal films or glass fiber-reinforced reinforcing elements of plastic in cable construction. An especially preferred use is, for example, direct coating of the central reinforcing element of optical cables. This central element can be coated with the nontacky version of the adhesive and then rolled up and put into intermediate storage. In ordinary optical cables the individual optical fiber conductors are arranged concentrically around this central element. After reactivation of the non-tacky version of the adhesive on the central element these optical conductors can be bonded directly to the central element and can then undergo additional manufacturing steps. Possibly the plastic tubes can contain the optical conductor(s), and can likewise be coated on the outside with the hot-melt adhesive in accordance with the invention. Encasing the optical conductors with a water-swellable multilayer adhesive ribbon or multilayer nonwoven material and additional longitudinal sealing of the hollow space between the central element and the tubes against water using a grease (petroleum jelly), which is necessary according to the current state of the art, can be omitted when using the hot-melt adhesives in accordance with the invention. In the cable construction the structurally required hollow space can be left out, since if there is penetration of water the water-swellable

hot-melt adhesive will completely fill this hollow space because of the swelling process and thus it will ensure a reliable longitudinal seal against water. This type of construction produces a simplified binding technology, the possibility of working without grease as well as a significant decrease of weight of the cable construction. In addition, compared to the processing of swellable nonwovens a higher production rate is possible.

With the surface-tacky version of the hot-melt adhesive in accordance with the invention it is applied directly in the cable construction line onto the simple element and/or the optical conductors and in this case a reactivation of the hot-melt adhesive is not necessary.

Figure 1 shows schematically the cross section through an optical cable using the swellable hot-melt adhesives in accordance with the invention. The central element 1 is surrounded by several tubes 2 containing optical conductors. An encasement 3 of the optical conductors with the swellable hot-melt adhesive was shown. Cable jacket 4 forms the outside enclosure of the cable.

The water-swellable hot-melt adhesives are made as follows:

Resin esters, ethylene/vinyl acetate and acrylate copolymers are melted together at 140 to 160°C and homogenized. Then the polydiol(s) is/are added and the mixture is homogenized. Then the polyvinyl methyl ether and the stabilizing agent are added and homogenized. Finally the powdered polyacrylic acid salt is incorporated and homogenized. With the blockfree versions the wax is then added lastly and homogenization is carried out one more time. Then the

homogeneous melt is put into the appropriate packaging units and cooled to room temperature.

The following test is carried out for a practical verification of the functional capability of the water-swellable hot-melt adhesive:

A 0.1 mm thick polyester film is coated on both sides with the hot-melt adhesive in a layer of 0.2 mm to a maximum of 0.4 mm per side. Here the total thickness of the layers of the coated film should not exceed 1 mm. This two-sided-coated film is wrapped around a Teflon bar (200 mm long, 19 mm in diameter), with a maximum overlapping of 2 mm on the longitudinal seam. A glass tube of an inside diameter of 23 mm and a length of 350 mm is provided at its lower outlet with a loose cotton plug, then the Teflon rod wrapped with the coated film is put into the center of the glass tube and the upper end of the vertically positioned glass tube is closed with another loose cotton plug. A dropping funnel containing 250 mL deionized water is positioned above the glass tube.

If now the water is allowed to slowly drip from above into the glass tube, the hot-melt adhesive will swell within a short time so that only during a brief initial phase will a few mL of water flow out of the glass tube. After that no additional water can penetrate.

The water-swellable hot-melt adhesive in accordance with the invention that was used for the above practical test had the following composition:

19.5 parts pentaerythritol ester of abietic acid
29.8 parts ethylene/vinyl acetate

10.0 parts copolymer of ethylene, acrylic acid, vinyl acetate and vinyl alcohol

0.2 part sterically hindered phenol as antioxidant

19.5 parts polyethylene glycol, molecular weight 12,000

20.0 parts sodium salt of polyacrylic acid (swelling agent)

1.0 part ethylene bisstearamide (antiblocking agent).

Claims

1. Water-swellable thermoplastic material for bonding and coating made from

A) A water-insoluble

B) A water-soluble or water-dispersible component and

C) A water-swellable component, which is characterized by the fact that component contains at least one water-insoluble (co)polymer and at least one additional resin, component B contains at least one water-soluble or dispersible oligomer and/or (co)polymer and component C consists of a water-swellable (co)polymer, where components A, B and C are homogeneously intermixed.

2. A material as in Claim 1, which is characterized by the fact that component A contains one or more resins with a saponification number*, at least one thermoplastic (co)polymer and possibly tackifying additives.

3. A material as in Claim 1, which is characterized by the fact that component A contains one or more resins with a saponification number, at least one thermoplastic (co)polymer and additives that reduce adhesiveness.

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* [Translator's note: i.e., that has a nonzero saponification number.]

4. A material as in Claims 1 to 3, which is characterized by the fact that the water-swellable (co)polymer in component C is a superabsorber from the group consisting of polyacrylic acid, polyacrylic acid salts, polyacrylamide or their copolymers, possibly with acrylonitrile, or graft polymers or copolymers of these with starch or cellulose.

5. A material as in Claim 1 to 4, which is characterized by the fact that the water-soluble or water-dispersible oligomer/(co)polymer of component B is chosen from the group consisting of polyethylene glycol, polyvinyl methyl ether, poylvinylpyrrolidone, water-soluble or water-dispersible polyesters or copolyesters, water-soluble or water-dispersible acrylate polymers.

6. The use of the water-swellable thermoplastic materials as in at least one of the preceding claims as a hot-melt adhesive and sealing material to make watertight constructions, especially to make longitudinally watertight cable constructions.